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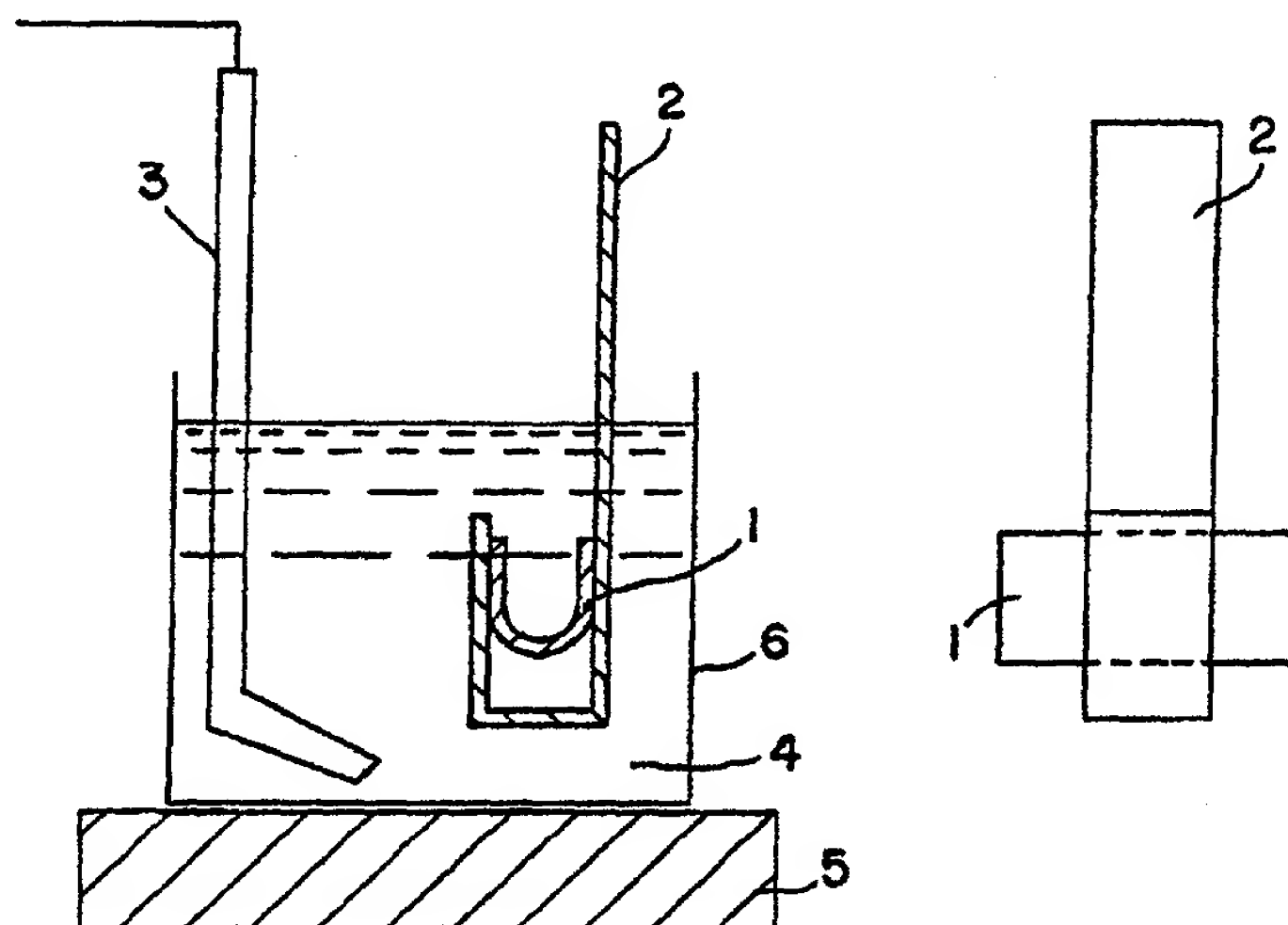
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(54) Title: ACIDIC CLEANING COMPOSITION AND PROCESS FOR ALUMINIFEROUS METALS



(57) Abstract

A surface of aluminiferous metal is cleaned of oil, grease, smut, and oxide on aluminum-containing metals, by contact for 10 to 80 seconds and preferably at 60 °C to 85 °C with an aqueous cleaning bath that has a pH no greater than 2.0, that contains a cleaning agent composition having (a) sulfuric acid, (b) nitrate ion, and (c) ferric ion at a weight ratio (a):(b):(c) of 50 to 400:5 to 50:0.2 to 5 and a ratio $[Fe^{+3}]/[FA]$, which is the ratio of the ferric ions concentration $[Fe^{+3}]$ to the free acidity $[FA]$, of no more than $7 \times 10^{-4}:1$, and that optionally also contains surfactant and surfactant stabilizer. This cleaning composition does not produce sludge even when diluted.

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Description**ACIDIC CLEANING COMPOSITION AND PROCESS FOR ALUMINIFEROUS METALS**Technical Field

This invention relates to acidic cleaning agent compositions useful for suitably etching and thereby cleaning the surface of articles, for example, beverage containers, made from aluminiferous metals and alloys. This invention also relates to cleaning processes that use such compositions. More specifically, the invention relates to a novel acidic cleaning agent composition for aluminiferous metals that is able — through its excellent capacity to remove the lubricant and forming oil adhering on the surface of aluminiferous metal and the black smut and oxide film that form on such surfaces — to generate a surface that is ideal for an ensuing conversion treatment. In addition, this novel acidic cleaning agent composition is very resistant to sludging, even when, during actual use, the cleaning agent becomes diluted through admixture with the process water for precleaning, rinsing, and the like. The invention also relates to a cleaning process that uses the said novel acidic cleaning agent composition.

Background Art

Containers of aluminum and aluminum alloy are typically fabricated by a forming operation that includes drawing and ironing ("drawing and ironing" being hereinafter usually abbreviated as the "draw-ironing" or "DI" process). This operation results in the deposition of lubricant and forming oil on the container surface and also causes the production thereon of aluminum oxide. The DI process additionally causes the adhesion of minute residual aluminum particles (denoted below as "smut") on the container surface, and in fact this smut is present in relatively large amounts on the interior surface of the container. As a result of these facts, when the aluminiferous metal container is to be submitted to a conversion treatment or painting operation, the surface of the container must be cleaned in order that contaminants detrimental to the ensuing treatments will not remain on the surface.

Acidic cleaning baths heretofore used for aluminum have consisted of sulfuric acid/hydrofluoric acid cleaning baths as well as these types of cleaning

baths supplemented with a small concentration of hexavalent chromium in order to inhibit equipment corrosion. However, these conventional acidic cleaning baths, by virtue of their content of complex fluoride ions and hexavalent chromium containing ions, create problems at the stage of effluent treatment, e.g., by imposing high loads on effluent treatment or by making it difficult to treat the effluent in practice. The provision of an acidic cleaning bath that does not contain these ions has therefore been desired.

This desire has been met, for example, by the cleaning baths disclosed in (a) Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 2-73983 [73,983/1990] and (b) Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 4-52289 [52,289/1992]. Cleaning bath (a) comprises phosphoric acid, a mineral acid such as sulfuric acid, an oxidizing agent, 0.02 to 0.170 grams per liter (hereinafter usually abbreviated as "g/L") of ferric ions, and surfactant. Cleaning solution (b) comprises oxidizing agent, 0.02 to 5 g/L of ferric ions, surfactant, at least one mineral acid selected from the group consisting of sulfuric acid, nitric acid, and phosphoric acid, and also glycol for the purpose of stabilizing the surfactant in the cleaning bath.

Each of these two treatment baths does exhibit distinctive features and they each exhibit a cleaning capacity worth noting within the realm of cleaning baths for aluminum. At the same time, however, cleaning bath (a) will produce aluminum phosphate sludge when its pH is raised, as a result of either accumulation of aluminum ions etched from the substrate as the bath ages or dilution of the bath by admixture into it of some of the process water for precleaning, rinsing, and the like during actual plant operations.

As a result of broad allowable range for ferric ions content in cleaning bath (b), there will be instances when this bath produces iron hydroxide sludge as a result of the pH increase that occurs when this bath is diluted by admixture with the process water for precleaning, rinsing, and the like. Production of this sludge creates operating problems such as adhesion to the heat exchanger and a reduced cleaning performance, due to clogging of spray nozzles, when this bath is used by spraying.

Disclosure of the InventionProblems to Be Solved by the Invention

The present invention provides an acidic cleaning agent composition for aluminiferous metals that avoids the problems described above for the prior art. More specifically, the present invention provides an acidic cleaning agent composition for aluminiferous metals that has an excellent capacity to clean off the grease, oil, smut, and oxide on the surface of aluminiferous metals to yield a clean surface and that has an excellent operating stability in that it resists sludge production even when diluted with rinse water or the like. The invention also provides a cleaning process employing this acidic cleaning agent composition.

Summary of the Invention

It has been determined that the above noted problems of prior art cleaning compositions, which for brevity are often alternately called "baths" hereinafter, even if used by some method other than immersion, could be avoided by using an aqueous composition comprising, preferably consisting essentially of, or more preferably consisting of sulfuric acid, nitrate ions, and ferric ions (and any necessary counterions if the electrical charges of the nitrate and ferric ions do not neutralize each other) as its essential components in addition to water; maintaining the pH at or below 2.0; restricting the $[Fe^{+3}]/[FA]$ ratio, where $[Fe^{+3}]$ is the ferric ions concentration in moles per liter (hereinafter usually abbreviated as "mol/L") and $[FA]$ is the free acidity exhibited by the aqueous solution, to a particular range of values; and, optionally, including surfactant and surfactant stabilizer in the bath.

An acidic cleaning agent composition according to the present invention for treatment of aluminiferous metals characteristically contains (a) sulfuric acid, (b) nitrate ions, and (c) ferric ions in a weight ratio (a) : (b) : (c) of 50 - 400 : 5 - 50 : 0.2 - 5 and has a ratio $[Fe^{+3}]/[FA]$, which denotes the ratio of the (c) ferric ions concentration $[Fe^{+3}]$ expressed in mol/L to the free acidity $[FA]$, of 7×10^{-4} or less. For the purposes of this description, the "free acidity" or "[FA]" is defined to be the number of milliliters of 0.1 N aqueous sodium hydroxide required to titrate an exactly 5 milliliter sample of the cleaning bath using phenolphthalein as indicator. The above description applies to either of two embodiments of the

invention: a working composition, suitable for direct use in cleaning, or a concentrate composition, which can be diluted with water to provide the above noted essential constituents of working composition in the same ratios as in the concentrate composition.

5 An aluminiferous metal cleaning process according to the present invention characteristically comprises cleaning the surface of aluminiferous metal by contacting the surface of aluminiferous metal for 10 to 80 seconds with an aqueous working cleaning bath containing the aforesaid cleaning agent composition and having a pH not exceeding 2.0 and thereafter rinsing the cleaned surface
10 with water.

Brief Description of the Drawings

Figure 1A is a front sectional view of the structure of the test apparatus for determining the development of pitting, and Figure 1B is a side projection view of the substrate and its support, which shows how the sample is supported in the
15 test apparatus.

Detailed Description of the Invention, Including Preferred Embodiments

In a preferred embodiment, an acidic cleaning agent working composition according to the present invention contains, in addition to the aforesaid (a) sulfuric acid, (b) nitrate ions, and (c) ferric ions, (d) surfactant and (e) surfactant stabilizer in a weight ratio (a) : (b) : (c) : (d) : (e) of 50 - 400 : 5 - 50 : 0.2 - 5 : 1 - 100
20 : 1 - 200.

In a preferred embodiment of the aluminiferous metal cleaning process according to the present invention, the aforesaid working cleaning bath contains from 5 to 40 g/L or preferably from 10 to 30 g/L of sulfuric acid, from 0.5 to 5 g/L or preferably from 1.0 to 3.0 g/L of nitrate ions, and from 0.02 to 0.5 g/L or preferably from 0.08 to 0.4 g/L of ferric ions.
25

In an independently preferred embodiment of the aluminiferous metal cleaning process according to the present invention, the aforesaid working cleaning bath is maintained during the process at a temperature of 60 °C to 85 °C and also contains 0.1 to 10 g/L of surfactant and 0.1 to 20 g/L of surfactant stabilizer.
30 Etching of the aluminiferous metal surface is prone to be inadequate at cleaning temperatures below 60 °C, which can result in a failure to completely remove the

oxide and smut on the metal surface. On the other hand, cleaning temperatures higher than 85 °C cannot be expected to yield additional cleaning effects, and are thus energy-wasting and economically fruitless. Moreover, when oxidizing agent and/or metal ions are present in the acidic cleaning bath according to the present invention for aluminiferous metals, raising the temperature of the cleaning bath more than necessary can result in the disadvantage of a reduced surfactant stability.

The surfactant in an aluminiferous metal cleaning composition or process according to the present invention is preferably selected from nonionic surfactants, and independently the surfactant stabilizer in an aluminiferous metal cleaning composition or process according to the present invention preferably is selected from the group consisting of alcohols with from 2 to 10 carbon atoms per alcohol molecule, including alcohols with more than one hydroxyl group and/or with one or more ether oxygen atoms per molecule in addition to the hydroxyl groups.

In a preferred embodiment of an aluminiferous metal cleaning process according to the present invention, the ferric ions concentration $[Fe^{+3}]$ in the cleaning bath is controlled during cleaning of the surface of aluminiferous metal with the subject cleaning bath by measuring the redox potential of the cleaning bath and adding oxidizing agent to the cleaning bath as needed, depending on the measured redox potential value.

With regard to the production of ferric hydroxide sludge that occurs when a sulfuric acid/iron cleaning agent is diluted by rinse solutions and the like, the inventors discovered that the production of this sludge depends on the balance between the free acidity of the subject aqueous solution and the ferric ions concentration, more specifically that the resistance to sludging can be improved by keeping the $[Fe^{+3}]/[FA]$ ratio (as defined above) at a value of 7×10^{-4} or less, preferably not more than 2.5×10^{-4} .

An acidic cleaning composition according to the present invention preferably contains (a) sulfuric acid, (b) nitrate ions, and (c) ferric ions in a weight ratio of 100 - 300 : 10 - 30 : 1.0 - 1.8 and independently preferably contains in addition (d) surfactant and (e) surfactant stabilizer in a weight ratio (a) : (b) : (c) : (d) : (e)

of 100 - 300 : 10 - 30 : 1.0 - 1.8 : 5 - 30 : 5 - 100.

5 An aluminiferous metal cleaning process according to the present invention normally comprises adjusting the pH of a working cleaning bath containing the aforesaid cleaning agent composition, optionally including surfactant and surfactant stabilizer, to 2.0 or less, cleaning the surface of aluminiferous metal by contacting such a surface for 10 to 80 seconds with the cleaning bath thus prepared, and thereafter rinsing the cleaned surface with water.

10 Contact between the cleaning bath and metal surface can be effected in the cleaning process according to the present invention by dipping the metal in the cleaning bath or by spraying or coating the cleaning bath onto the metal surface. The said spraying and coating processes can in each case be executed as continuous, single-step processes or as sequential multistage processes having two or more stages. Whatever the method of contact, the total contact time between cleaning bath and metal surface is preferably 10 to 80 seconds.

15 A process according to the present invention may include adjustment of the working cleaning bath containing the above-described cleaning agent composition (a concentrate cleaning agent composition is typically diluted with water to a specified concentration) and the optional addition thereto of surfactant and surfactant stabilizer.

20 When the sulfuric acid (H_2SO_4) proportion in the composition falls below the range specified above for a cleaning agent composition according to the present invention, the resulting cleaning bath usually will have an inadequate reactivity with the metal surface, which results in an incomplete etch of the aluminiferous metal surface and a failure to completely remove the oxide and smut that are produced during forming operations. Since the cleaning activity no longer improves at sulfuric acid proportions in excess of the above-specified range, exceeding the specified range serves simply to raise the cost of the cleaning bath and is therefore economically undesirable.

25 Nitric acid or a salt such as sodium nitrate, ammonium nitrate, and the like can be used as the source of the nitrate ions in the cleaning agent composition according to the present invention.

The nitrate ions content in a cleaning agent composition according to the

present invention preferably should be from 5 to 50 weight parts and more preferably is 10 to 30 weight parts of nitrate ions, in each case per 50 to 400 weight parts of sulfuric acid. The use of nitrate ions below this range will not usually provide a thorough inhibition of the pitting corrosion of aluminiferous metals that is produced when the cleaning bath contains chloride ions (from the bath make-up water) or copper ions that may be eluted from aluminum alloys. Since no additional improvement in cleaning activity is obtained for the use of nitrate ions beyond the specified range, such additions are economically undesirable because they both raise the cost of the cleaning bath and increase the cost of effluent treatment.

The ferric ions source for preparation of a cleaning bath or concentrate according to the invention can be a ferric salt, for example, of sulfuric acid, nitric acid, etc., or a ferrous salt, for example, of sulfuric acid, nitric acid, or the like, which is then oxidized with an oxidizing agent such as a nitrite salt, hydrogen peroxide, or the like to provide ferric ions. Ferric or ferrous salts of sulfuric acid and/or nitric acid are preferably used as the source of ferric ions in a cleaning agent composition according to the present invention. During the course of actual use, ferric ions are reduced to ferrous ions by the aluminum etching reaction. Therefore, the concentration of ferric ions will not remain at the desired value unless additional oxidizing agent is added during use of a working composition according to the invention. In such a situation, the redox potential of the cleaning bath can be measured and the treatment bath can be supplemented with oxidizing agent as needed to maintain the ferric ions concentration, as indirectly measured by the redox potential, within a desired range.

The corrosion of stainless steel cleaning and transport equipment is only weakly inhibited if the ferric ions proportion falls below the specified range in a working cleaning bath, particularly if the ferric ions concentration in the cleaning bath falls below 0.02 g/L. Specifically, the hold-down conveyor in aluminum can spray cleaners is only poorly protected from corrosion under these conditions and stainless steel conveyors will therefore undergo corrosion.

On the subject of the upper limit for the proportion of ferric ions, the production of iron hydroxide sludge is inhibited when the $[\text{Fe}^{+3}]/[\text{FA}]$ ratio does not

exceed 7×10^{-4} . In addition, the benefit from the presence of ferric ions also fails to increase further at large additions, and as a result the ferric ions content preferably should be kept at no more than 5 weight parts per 50 to 400 weight parts of sulfuric acid and independently preferably at a concentration in the treatment bath of no more than 0.5 g/L.

Surfactant and surfactant stabilizer can be added on an optional basis in the invention process when a working cleaning bath is prepared from a concentrate composition according to the invention. The surfactant preferably is selected from the group consisting of surfactants having a chemical structure that can be achieved by adducting ethylene oxide alone, or both ethylene and propylene oxides, with (i) an alcohol or alkyl phenol, preferably one having from 12 to 20 carbon atoms per molecule or (ii) abietic acid, with (i) preferred. The surfactant concentration in a working bath according to the invention is preferably 0.1 to 10 g/L and is more preferably 0.5 to 3 g/L. Only an insignificant improvement in cleaning capacity will normally be obtained at concentrations below 0.1 g/L. No additional improvement in cleaning capacity is usually obtained by addition of surfactant in excess of 10 g/L, and such high concentrations are therefore economically undesirable.

Propyl alcohol, butyl alcohol, propylene glycol, ethylene glycol, diethylene glycol, triethylene glycol, and the like, are all effective as the surfactant stabilizer in a composition according to the invention. The surfactant stabilizer may be a single alcohol or a mixture of two or more different alcohols. The surfactant stabilizer is preferably present at a concentration from 0.1 to 20 g/L of cleaning bath and more preferably at from 0.5 to 10 g/L of cleaning bath.

A surfactant stabilizer present in an acidic cleaning bath according to the invention is believed to function to improve the durability of the cleaning capacity of the bath by substantially inhibiting decomposition of the surfactant by polyvalent metal ions and oxidizing agent(s). A satisfactory stabilization of the surfactant is not usually obtained when the surfactant stabilizer is present at less than 0.1 g/L. No additional stability is obtained by the presence of amounts of surfactant stabilizer in excess of 20 g/L, and such concentrations are therefore economically undesirable.

An acidic cleaning bath used by the process according to the present invention may also contain a chelating agent that will complex aluminum ions, in order thereby to counter the decline in cleaning efficiency caused by aluminum elution during cleaning operations. Chelating agents suitable for this purpose are, for example, citric acid, oxalic acid, tartaric acid, gluconic acid, and the like.

A cleaning bath used by the process according to the present invention for cleaning aluminiferous metals has an excellent capacity to produce a clean surface on aluminiferous metal by removing the oil, grease, smut, and oxide therefrom. In addition, this cleaning bath provides for an excellent operating stability through its ability to resist sludge formation even when diluted.

Examples

A preferred process example described below employs a cleaning bath according to the present invention:

- (1) preliminary cleaning;
- (2) surface cleaning: degreasing (use of treatment bath according to the present invention);
treatment temperature: 60 °C to 85 °C
treatment technique: dipping or spraying
treatment time: 10 to 80 seconds
- (3) water rinse;
- (4) conversion coating forming treatment (either chromate or non-chromate);
- (5) water rinse;
- (6) deionized water rinse;
- (7) drying.

As used herein, the cleaning time in the process according to the present invention refers to the period of time during which the cleaning bath is in actual contact with the metal surface. Suitable cleaning times are preferably 10 to 80 seconds, while times of about 30 to 50 seconds are even more preferred. Contact times below 10 seconds can cause such problems as an inadequate oil and grease removal and/or an inadequate etching of the metal surface, resulting in a poor degreasing performance and/or an inadequate removal of oxide and smut from the metal surface. The cleaning effect becomes saturated at contact times

in excess of 80 seconds, and such contact times are thus economically undesirable.

The sample materials and test methods used in the working and comparative examples are described below.

5 **(1) Sample test substrates**

The tests were run on aluminum alloy (Type A3004) sheet with a thickness of 0.3 millimeter (hereinafter usually abbreviated as "mm") and on aluminum alloy DI cans fabricated therefrom by DI processing. DI lubricating oil and smut were adhered on this aluminum alloy DI can. (Mineral oil-based coolants and synthetic oil-based coolants have generally been used as the lubricant in aluminum DI can fabrication processes. Waterborne coolants have, however, recently entered into use to some degree. These waterborne coolants are more easily removed by cleaning operations. The tests described herein were run with a synthetic oil-based coolant, which is relatively resistant to cleaning, in order to clarify the utility of the present invention.)

15 **(2) Surfactants and Surfactant Stabilizers**

The following abbreviations are used in the tables below to identify the surfactants and surfactant stabilizers used, which had chemical natures as follows (EO = ethylene oxide; PO = propylene oxide; and numbers prefixed before EO or PO indicate moles of the EO and/or PO used per mole of the base material with an active hydrogen atom stated in the description):

20 Surfactant 1 was nonylphenol+18 EO adduct (hydrocarbon derivative).

Surfactant 2 was higher alcohol+5 EO+10 PO adduct (hydrocarbon derivative).

Surfactant 3 was nonylphenol+14 EO adduct (hydrocarbon derivative).

25 Surfactant 4 was higher alcohol+5 EO+15 PO adduct (hydrocarbon derivative).

Stabilizer 1 was propylene glycol.

Stabilizer 2 was ethylene glycol.

Stabilizer 3 was diethylene glycol.

Stabilizer 4 was n-propyl alcohol.

30 **(3) Test methods**

(A) Cleaning performance

(A-1) Corrosion resistance

Since the corrosion resistance is very sensitive to the degree of cleaning of the aluminum DI can, the extent of degreasing can be estimated from the cor-

rosion resistance after conversion treatment. The corrosion resistance was itself evaluated through the resistance to blackening by boiling water. The resistance to blackening by boiling water was measured by dipping the surface treated aluminum DI can in boiling tap water for 30 minutes and then visually rating the discoloration (blackening) thereby produced. The results were rated according to the following scale:

++ : no blackening + : partial blackening

x : blackening of entire surface

(A-2) Degree of desmutting

Smut was collected using the same cellophane tape from three sites (one upper, one middle, and one lower site) on the inner wall surface of a sample can. This tape was then applied on white paper (copy paper), and the degree of smut removal was rated by measurement using an SM-3 color computer from Suga Test Instruments Company, Limited. The test results are reported according to the following scale:

++ : L value greater than or equal to 80

+ : L value from 70 (inclusive) to 80 (exclusive)

x : L value less than 70

(B) Pitting test

In order to accelerate etching of the test specimen, which was a 50 mm x 80 mm aluminum coupon with a thickness of 0.3 mm, apparatus as shown in drawing Figures 1A and 1B was used. The test specimen 1 was bent into a U-shape and held in that shape in a support 2 made from a long strip of Type 316 stainless steel. This assembly was then immersed for 10 minutes in 1 liter of test bath 4 contained in a beaker 6 and heated to 75 °C by an immersion heater 3. The beaker was supported on magnetic rotor platform 5, so that the bath could be stirred during the immersion of the test specimen therein by a magnetic stirring bar (not shown). This immersion was followed by a water rinse and drying and then visual evaluation of pitting of the test specimen, using a microscop at low magnification. The absence of pitting was rated as "+ +" and the occurrence of pitting was rated as "x".

(C) Sludge production

Samples with eight degrees of dilution, specifically 50 ×, 100 ×, 150 ×, 200 ×, 300 ×, 500 ×, 1000 ×, and 3000 ×, were prepared from the test treatment baths, using tap water as the diluent. These were then held for 3 days at room temperature and the development of sludge was determined by noting any diminution of the Fe or Al concentrations in the samples. The appearance was also inspected after 7 days. The absence of sludge production was rated as "+ +" and the production of sludge was rated as "x".

(D) Maintenance of surfactant concentration in the acidic cleaning bath

Test treatment bath was heated to 75 ± 1 °C and held at quiescence, and a hydrogen peroxide concentration of 0.5 g/L in the bath was maintained with replenishment of the decomposed H_2O_2 . The residual amount of surfactant in the quiescent acidic bath was measured after 48 hours.

Examples 1 to 7 and Comparative Examples 1 to 5

Aqueous cleaning baths with the compositions reported in Tables 1 and 2 were prepared in Examples 1 to 7 and Comparative Examples 1 to 5 respectively. In each case, the aqueous treatment bath was heated to the cleaning temperature reported in Table 1 or Table 2 and sprayed onto the surface of the test substrate to effect contact for the time reported in Table 1 or 2.

The cleaned substrate material was thoroughly rinsed with tap water and then submitted to conversion treatment using a commercially available conversion treatment agent (Alodine® 404, from Nihon Parkerizing Company, Limited). The resulting conversion coating layer was subsequently rinsed with tap water, sprayed with deionized water (resistivity at least 3,000,000 ohm-cm), and dried in a hot-air drying oven at 180 °C for 2 minutes.

The test results are reported in Table 3. As these results make clear, the acidic cleaning baths in Examples 1 to 7 according to the present invention gave an excellent cleaning performance (corrosion resistance, desmutting), pitting inhibition, and sludging inhibition. Moreover, there was little surfactant decomposition in these baths. In contrast, none of the acidic cleaning baths in Comparative Examples 1 to 5, each of which was outside the scope of the present invention, gave an acceptable performance.

Table 1

Example Number	Characteristics of the Working Cleaning Composition					
	g/L of H ₂ SO ₄	Nitrate Ions		Ferric Ions		[Fe ⁺³]/ [FA] Ratio
		g/L	Source	g/L	Source	
1	10	1.0	HNO ₃	0.08	Fe ₂ (SO ₄) ₃	1.4×10^{-4}
2	15	2.0	HNO ₃	0.15	Fe ₂ (SO ₄) ₃	1.7×10^{-4}
3	20	3.0	HNO ₃	0.18	Fe ₂ (SO ₄) ₃	1.5×10^{-4}
4	15	1.0	HNO ₃	0.10	Fe(NO ₃) ₃	1.2×10^{-4}
5	15	1.0	NaNO ₃	0.15	Fe(NO ₃) ₃	1.7×10^{-4}
6	15	2.0	HNO ₃	0.15	Fe(SO ₄)*	1.7×10^{-4}
7	30	1.0	HNO ₃	0.40	Fe ₂ (SO ₄) ₃	2.0×10^{-4}

Footnote for Table 1

*Also contained an original addition of 0.10 g/L of hydrogen peroxide to oxidize ferrous to ferric ions.

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Table 1 continued

Example Number	Characteristics of the Working Compositions					
	Surfactant		Surfactant Stabilizer		Process Conditions	
	Type(s)	g/L	Type(s)	g/L	Temp., °C	Time, Sec.
1	Surfactant 1 Surfactant 2	1.0 1.0	Stabilizer 1	2.0	70	50
2	Surfactant 1 Surfactant 2 Surfactant 3	1.0 1.0 1.0	Stabilizer 2	2.0	65	50
3	Surfactant 3 Surfactant 4	1.0 1.0	Stabilizer 3	2.0	65	30
4	Surfactant 1 Surfactant 2	1.0 1.0	Stabilizer 1	2.0	75	60
5	Surfactant 1 Surfactant 2 Surfactant 3	1.0 1.0 1.0	Stabilizer 4	2.0	70	50
6	Surfactant 1 Surfactant 4	1.0 1.0	Stabilizer 1	2.0	70	50
7	Surfactant 1 Surfactant 2 Surfactant 3	1.0 1.0 1.0	Stabilizer 2	2.0	70	50

Table 2

Comparative Example Number	Characteristics of the Working Cleaning Composition					
	g/L of H ₂ SO ₄	Nitrate Ions		Ferric Ions		[Fe ³⁺]/[FA] Ratio
		g/L	Source	g/L	Source	
1	2.0	1.0	HNO ₃	0.20	Fe ₂ (SO ₄) ₃	1.4 × 10 ⁻³
2	10	0	none	0.15	Fe ₂ (SO ₄) ₃	2.7 × 10 ⁻⁴
3	8.0	0.1	HNO ₃	0	none	0
4	15	1.0	HNO ₃	1.3	Fe ₂ (SO ₄) ₃	1.5 × 10 ⁻³
5	15	2.0	HNO ₃	1.0	Fe(SO ₄)*	1.2 × 10 ⁻³

... This table is continued below ...

Example Number	Characteristics of the Working Compositions					
	Surfactant		Surfactant Stabilizer		Process Conditions	
	Type(s)	g/L	Type(s)	g/L	Temp., °C	Time, Sec.
1	Surfactant 1 Surfactant 2	1.0 1.0	Stabilizer 1	2.0	75	60
2	Surfactant 3	0.05	Stabilizer 3	2.0	70	60
3	Surfactant 2 Surfactant 3	1.0 1.0	Stabilizer 2	2.0	70	50
4	Surfactant 1 Surfactant 2	1.0 1.0	Stabilizer 1	2.0	50	40
5	Surfactant 1 Surfactant 2	1.0 1.0	none	-	75	50

Footnotes and Abbreviation for Table 2

*Also contained an original addition of 1.0 g/L of hydrogen peroxide to oxidize ferrous to ferric ions.

Temp. = Temperature; Sec. = Seconds

Table 3

Example or Comparative Example No.	Cleaning Performance		Pitting Inhibition	Inhibition of Sludging	Residual Surfactant
	Cor. Res.	Desmutting			
Example 1	++	++	++	++	90 %
Example 2	++	++	++	++	87 %
Example 3	++	++	++	++	90 %
Example 4	++	++	++	++	89 %
Example 5	++	++	++	++	85 %
Example 6	++	++	++	++	85 %
Example 7	++	++	++	++	85 %
Com. Ex. 1	x	x	++	x	90 %
Com. Ex. 2	x	x	x	++	90 %
Com. Ex. 3	+	+	x	++	90 %
Com. Ex. 4	+	+	++	x	90 %
Com. Ex. 5	++	++	++	x	43 %

Abbreviations for Table 3

Cor. Res. = Corrosion Resistance; Com. Ex. = Comparative Example.

The following problems were encountered in the comparative examples.

Comparative Example 1: Due to its low free acidity, sludge was produced and its cleaning performance was also poor.

Comparative Example 2: Due to its deficiency in nitrate ions, the cleaning performance and pitting inhibition in this comparative example were poor.

Comparative Example 3: Due to its deficiency in nitrate ions and ferric ions, the cleaning performance and pitting inhibition in this comparative example were poor.

Comparative Examples 4 and 5: Sludge was produced because the value of $[Fe^{+3}]/[FA]$ was greater than 7×10^{-4} . In addition, in Comparative Example 5, the residual surfactant was very low because of the lack of a surfactant stabilizer.

Benefits of the Invention

An acidic cleaning bath according to the present invention has an excellent capacity to provide a clean surface by removing the oil, grease, smut, and oxide present on the surface of aluminiferous metals. The operating stability is strongly enhanced because production of sludge is highly inhibited even after dilution by rinse water or other sources of additional water.

Claims

1. An aqueous acidic cleaning agent composition for aluminiferous metals, said composition comprising water, (a) sulfuric acid, (b) nitrate ions, and (c) ferric ions in a weight ratio (a) : (b) : (c) of 50 - 400 : 5 - 50 : 0.2 - 5 and having a ratio $[\text{Fe}^{+3}]/[\text{FA}]$, which denotes the ratio of the ferric ions concentration $[\text{Fe}^{+3}]$ expressed in mol/L to the free acidity $[\text{FA}]$, that is not more than 7×10^{-4} .
2. An acidic cleaning agent composition according to claim 1, additionally comprising (d) surfactant and (e) surfactant stabilizer in a weight ratio (a) : (b) : (c) : (d) : (e) of 50 - 400 : 5 - 50 : 0.2 - 5 : 1 - 100 : 1 - 200.
3. An acidic cleaning agent composition according to claim 2, wherein the weight ratios of components (a) : (b) : (c) : (d) : (e) are 100 - 300 : 10 - 30 : 1.0 - 1.8 : 5 - 30 : 5 - 100.
4. An acidic cleaning agent composition according to claim 3, wherein the ratio $[\text{Fe}^{+3}]/[\text{FA}]$ is not more than 2.5×10^{-4} .
5. A process for cleaning a surface of an aluminiferous metal, comprising steps of:
 - (I) contacting the surface of aluminiferous metal for 10 to 80 seconds with an aqueous cleaning bath containing components (a), (b), (c), (d), and (e) in the ratios as recited in any one of claims 2 - 4 and having a pH not exceeding 2.0; and
 - (II) thereafter discontinuing contact between the surface and the aqueous cleaning bath and rinsing the cleaned surface with water.
6. A process according to claim 5, wherein the aqueous cleaning bath contains 5 to 40 g/L of sulfuric acid, 0.5 to 5 g/L of nitrate ions, 0.02 to 0.5 g/L of ferric ions, from 0.1 to 10 g/L of surfactant, and from 0.1 to 20 g/L of surfactant stabilizer.
7. A process according to claim 6, wherein the aqueous cleaning bath contains 10 to 30 g/L of sulfuric acid, 1.0 to 3.0 g/L of nitrate ions, 0.08 to 0.4 g/L of ferric ions, from 0.1 to 10 g/L of surfactant, and from 0.5 to 3.0 g/L of surfactant stabilizer.

8. A process according to claim 7, wherein the surfactant is selected from the group consisting of ethoxylates and both ethoxylates and propoxylates of alcohols and alkyl phenols having from 12 to 20 carbon atoms per molecule of the alcohols and alkyl phenols and the surfactant stabilizer is selected from the group consisting of alcohols and ether alcohols having from 2 to 10 carbon atoms per molecule of the alcohols and ether alcohols.

9. A process according to any of claims 6 to 8, wherein the aqueous cleaning bath is maintained during step (I) at a temperature of 60 °C to 85 °C.

10. A process according to claim 9, wherein the concentration of ferric ions in the aqueous cleaning bath is maintained within a prescribed range by measuring the redox potential in the aqueous cleaning bath and adding to the aqueous cleaning bath oxidizing agent as needed to maintain the ferric ions concentration, as indirectly measured by the redox potential, within the prescribed range.

11. A process for cleaning a surface of an aluminiferous metal, comprising steps of:

- (I) contacting the surface of aluminiferous metal for 10 to 80 seconds with an aqueous cleaning bath containing components (a), (b), and (c) in the ratios as recited in claim 1 and having a pH not exceeding 2.0; and
- (II) thereafter discontinuing contact between the surface and the aqueous cleaning bath and rinsing the cleaned surface with water.

12. A process according to claim 11, wherein the aqueous cleaning bath contains 5 to 40 g/L of sulfuric acid, 0.5 to 5 g/L of nitrate ions, and 0.02 to 0.5 g/L of ferric ions.

13. A process according to claim 12, wherein the aqueous cleaning bath contains 10 to 30 g/L of sulfuric acid, 1.0 to 3.0 g/L of nitrate ions, 0.08 to 0.4 g/L of ferric ions, from 0.1 to 10 g/L of surfactant, and from 0.5 to 3.0 g/L of surfactant stabilizer.

14. A process according to claim 13, wherein the surfactant is selected from the group consisting of ethoxylates and both ethoxylates and propoxylates of alcohols and alkyl phenols having from 12 to 20 carbon atoms per molecule of the

alcohols and alkyl phenols and the surfactant stabilizer is selected from the group consisting of alcohols and ether alcohols having from 2 to 10 carbon atoms per molecule of the alcohols and ether alcohols.

5 15. A process according to any of claims 11 to 14, wherein the aqueous cleaning bath is maintained during step (I) at a temperature of 60 °C to 85 °C.

10 16. A process according to claim 15, wherein the concentration of ferric ions in the aqueous cleaning bath is maintained within a prescribed range by measuring the redox potential in the aqueous cleaning bath and adding to the aqueous cleaning bath oxidizing agent as needed to maintain the ferric ions concentration, as indirectly measured by the redox potential, within the prescribed range.

FIG. 1A

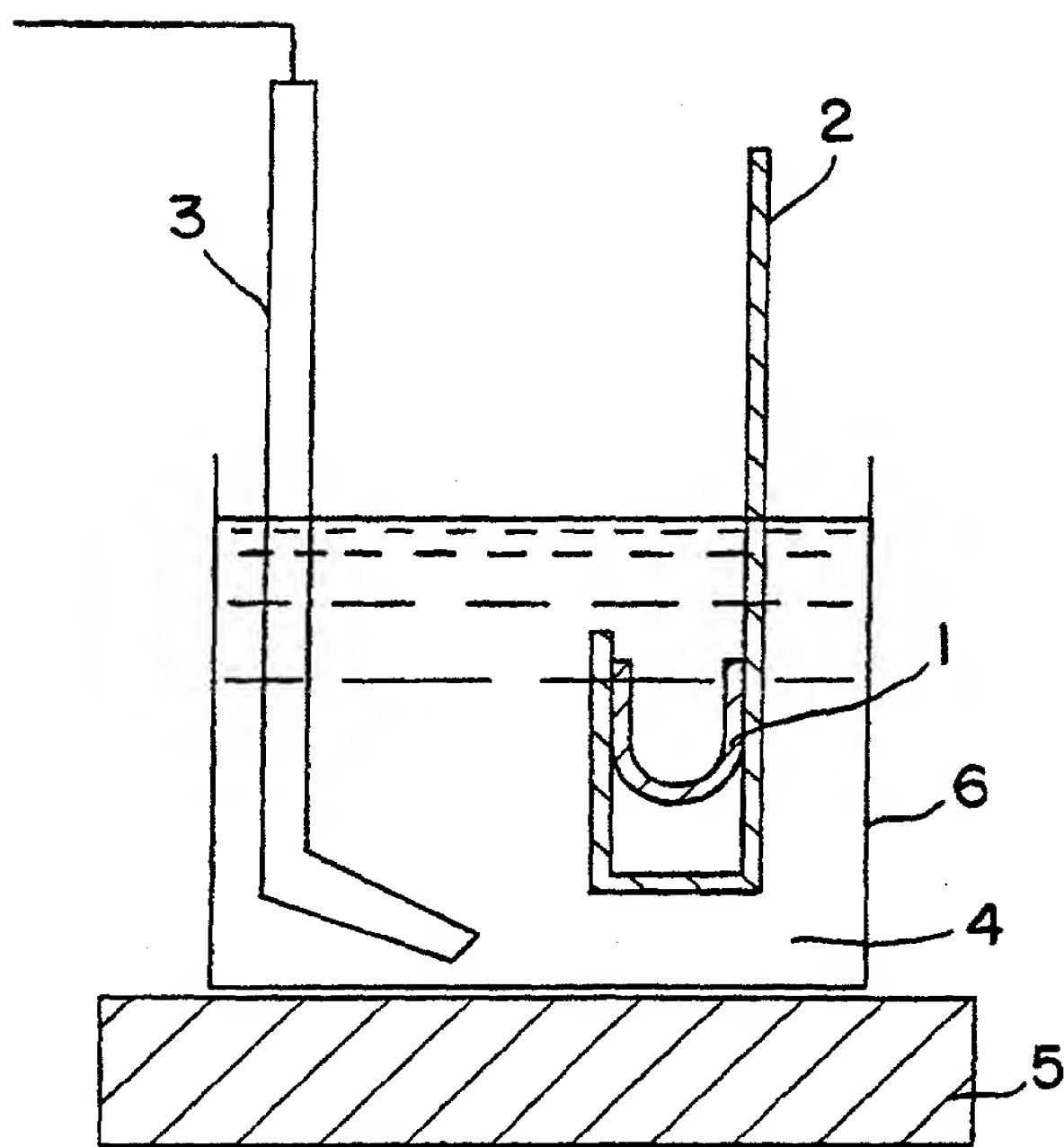
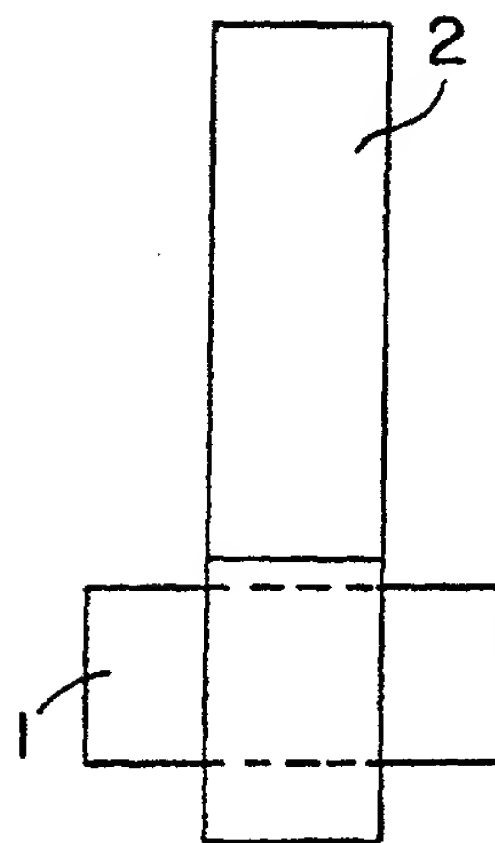


FIG. 1B



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/07545

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B08B 3/08; C09K 13/04, 13/06; C11D 7/08; C23G 1/02, 1/08

US CL : 134/3, 41; 252/79.2, 79.4; 510/245, 254, 269, 270, 271

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 134/3, 41; 252/79.2, 79.4; 510/245, 254, 269, 270, 271

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

search terms: sulfuric acid, nitrate, ferric, ion, nitric acid, surfactant

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,336,425 (AOKI ET AL) 09 August 1994, See Abstract; col. 2, line 1 to col. 4, line 15.	1-16
X	US, A, 5,393,447 (CARLSON ET AL) 28 FEBRUARY 1995, See Abstract; col. 2, lines 5-48; col. 3 line 5 to col. 4, line 65.	1-16
X	US, A, 4,886,616 (YAMASOE ET AL) 12 December 1989; See Abstract; col. 1, line 40 to col. 4, line 30.	1-16
X	US, A, 4,959,105 (NEIDIFFER ET AL) 25 September 1990, See Abstract; col. 2, lines 35-69; col. 4, lines 1-15; col. 6, lines 1-69; col. 7, lines 50-69.	1-16

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

15 AUGUST 1996

Date of mailing of the international search report

13 NOV 1996

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/07545

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,116,713 (OTRHALEK ET AL) 26 September 1978, See Abstract; col. 2, lines 30-69; col. 3, line 13 to col. 4, line 50.	1-16

FIG. 1A

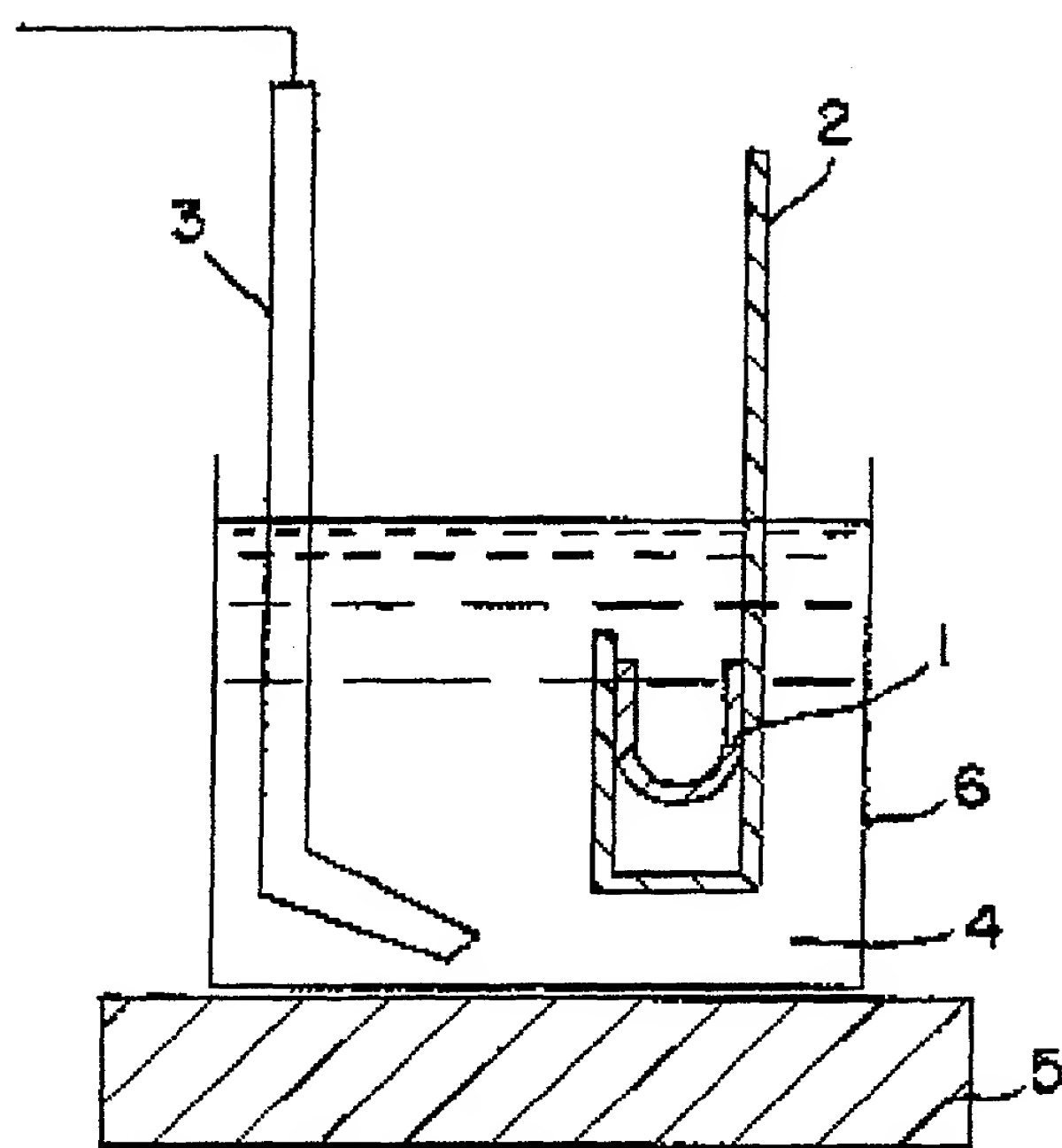


FIG. 1B

